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RESEARCH AND APPLICATIONS BRANCH
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LIST OF ACRONYMS

AED	Atomic Emission Detector
C&P	Conservation and Protection
CAPCO	Canadian Association of Pesticide Control Officials
CCIW	Canada Centre for Inland Waters
CEPA	Canadian Environmental Protection Act
CHCL	Clean and Hazardous Chemical Laboratory
CI	Chemical Ionization
CPPA	Canadian Pulp and Paper Association
CRM	Certified Reference Material
DNA	Deoxyribonucleic Acid
DOE	Department of the Environment
DQAC	Dioxin Quality Assurance Committee
ECD	Electron Capture Detector
EI	Electron Impact
EP	Environmental Protection
EPA	Environmental Protection Agency
ESRF	Environmental Studies Research Fund
FIA	Flow Injection Analysis
FICP	Federal Interdepartmental Committee on Pesticides
FP	Federal-Provincial
FTB	Floating Tire Breakwater
GC/MS	Gas Chromatography/Mass Spectrometry
GLC	Gas Liquid Chromatography
GLERL	Great Lakes Environmental Research Laboratory
HPLC	High Pressure Liquid Chromatography
HRGC	High Resolution Gas Chromatography
IA	Immunoassay
ICAP	Inductively Coupled Argon Plasma
IJC	International Joint Commission
IRQC	Interregional Quality Control
IWD	Inland Waters Directorate
LC	Liquid Chromatography
LC/MS	Liquid Chromatography/Mass Spectrometry
LC_{50}	Lethal Concentration for 50% of test population
LRB	Lakes Research Branch
LRTAP	Long Range Transport of Atmospheric Pollutants
LSE	Large Sample Extraction
MOE	Ontario Ministry of the Environment
MS/MS	Mass Spectrometry/Mass Spectrometry
NICI	Negative Ion Chemical Ionization
NRCC	National Research Council Council
NWQL	National Water Quality Laboratory

List of acronyms (continued)

NWRI	National Water Research Institute
PAH	Polynuclear Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PCDD	Polychlorinated Dibenzo-p-dioxin
PCDF	Polychlorinated Dibenzofuran
PESTMYOP	Pesticide Multi-year Operational Plan
PFB	Pentafluorobenzyl
PID	Photoionization Detector
ppq	Part per Quadrillion (10^{-15})
ppt	Part per Trillion (10^{-12})
PPWB	Prairie Provinces Water Board
QA	Quality Assurance
QC	Quality Control
RAB	Research and Applications Branch
RFA	Resin and Fatty Acids
RIA	Radioimmunoassay
RM	Reference Material
RRB	Rivers Research Branch
RSD	Research Support Division
SFC	Supercritical Fluid Chromatography
SFE	Supercritical Fluid Extraction
SWADE	Surface Wave Dynamics Experiment
SWAPP	Surface Wave Processes Program
TCDD	Tetrachlorodibenzo-p-dioxin
TDD	Tyramine Dioxin Derivative
TMA	Texel-Marsden-Arsloe
WAWSP	Wave and Wave Stress Prediction
WQB	Water Quality Branch
WRB	Water Resources Branch
WSC	Water Survey of Canada

PREAMBLE

In keeping with our established practice, it is my pleasure to present to our clients, collaborators and colleagues this annual report covering the activities of the Research and Applications Branch, National Water Research Institute, for the period April 1, 1989 to March 31, 1990.

This document contains an overview of the projects and activities underway in the Branch, followed by study reports highlighting the results achieved during the past year. Readers interested in obtaining additional information or providing comments on any particular study are invited to contact the appropriate study leader or the Branch Director's Office.

John Lawrence
Director

RESEARCH AND APPLICATIONS BRANCH

J. Lawrence, Director

OVERVIEW

The Research and Applications Branch (RAB) is one of the three research branches of the National Water Research Institute (NWRI). The mission oriented research activities carried out by the Branch are grouped into three projects, namely Analytical Chemistry Research, Quality Assurance and Hydraulics Studies. In the following pages of this report, a general overview of each project is provided as well as a progress report on each study currently under way.

Within the Branch's mandate, sensitive and cost effective analytical methods are developed for the measurement of priority chemical and biochemical parameters. The Branch also has lead responsibility for analytical data quality for many C&P programs. New knowledge of the dynamics of water is sought to provide a framework for the management of water resources and for biology and chemistry research in aquatic ecosystems. The interfaces between water and the atmosphere, bottom sediments and shores are studied to explain the mechanisms controlling the transport of pollutants and erosion. The research focusses on enhancing the science base of Environment Canada's priority programs. Many of our studies are in direct support of the implementation of the Canadian Environmental Protection Act (CEPA), while others make significant contributions to programs such as Long Range Transport of Atmospheric Pollutants, Great Lakes Water Quality, Federal/Provincial Water Quality and Climate Change.

Major clients for the output of the Branch activities include other Branches within the Institute, National and Regional laboratories of the Water Quality Branch and Environmental Protection, the Water Resources Branch, Provinces and the Private Sector.

The Branch is continuing to maintain and, where feasible, increase the level of technology transfer with the university and private industry sectors. Technology developed and capabilities available in the Branch were featured as part of the NWRI participation at the GLOBE '90 Trade Fair held in Vancouver, B.C. in March 1990. The Branch offers a wide range of specialized equipment, services and facilities that can be used or accessed by external parties with full or partial cost recovery, in accordance with the Treasury Board guidelines.

ANALYTICAL CHEMISTRY RESEARCH PROJECT

I. Sekerka, Project Chief

INTRODUCTION

The main objectives of the Analytical Chemistry Project of the Research and Applications Branch are: to develop new and improved analytical methods as well as screening and sampling procedures which are accurate, cost-effective, sensitive and unambiguous for the identification and quantification of contaminants in aquatic ecosystems; to play a lead role in documentation, validation and standardization of analytical methodologies to ensure accuracy and reliability of analytical data; to provide NWRI with sophisticated instrumentation and facilities; and to transfer developed methods and technologies to the national and regional laboratories of Conservation and Protection and a wide variety of other "clients".

HIGHLIGHTS

Promising results have been obtained from studies focussed on the pre-concentration, clean-up and separation steps of analytical methods.

- Supercritical fluid extraction has been successfully coupled to a high resolution gas chromatography - electron capture detector system. In comparison with conventional extraction procedures using organic solvents, this approach gives significantly improved extraction efficiencies of analytes such as PCBs and dioxins. The system also has the added advantage of a many fold reduction in the time required for the extraction step.

- As part of the research toward the development of a radioimmunoassay for the screening of dioxins in environmental samples, a multilayer column chromatography method for general application in the extraction and clean-up of samples analysed for polychlorinated dibenzodioxins has been fully evaluated and found to compare very favourably in terms of effectiveness and efficiency with the traditional liquid phase extraction procedure.

- The successful performance obtained in field and laboratory experiments with the large sample extractor developed earlier under this Project has spurred the interest of a small private sector firm to produce a commercial version of the apparatus.

This extraction technology and a prototype robotic system used for sample introduction in automated analytical methodologies were publicly displayed as part of Environment Canada's exhibits at the GLOBE '90 Trade Fair, held in Vancouver in March 1990.

Studies aimed at developing new or improved techniques for the detection, identification or determination of particular compounds of interest have resulted in numerous signficiant accomplishments:

- Analtyical methods incorporating a continuous flow iso-thermal distillation step have been developed for the amperometric or conductometric determination of ammonia and cyanide in aqueous samples. An ingenious system of valves has been perfected to permit in-line pretreatment of the samples and shown to contribute significantly to the efficiency and reliability of the methods through the elimination of manual sample preparation steps.

- A gas chromatography - atomic emission detector system has been used successfully for the detection of various organic compounds containing hetero atoms, such as phosphorus, sulfur and nitrogen, in samples collected during the tainted fuels and tire fire environmental emergency incidents. This approach will be investigated further with other compounds and its potential evaluated as part of broad spectrum analysis protocols.

- A sensitive method has been developed for the determination and confirmation of resin and fatty acids present in pulp and paper mill effluents and provides a valuable contribution to the characterization of these industrial discharges. The main features of the method consist of the transformation of the acids into ester derivatives and their quantitative determination by mass spectrometry. The method was used in a recent survey of selected pulp and paper mill effluents collected from across Canada.

- An ion chromatography method has been developed for the determination of seventeen organic and inorganic acids suspected of being present in precipitation samples.

QUALITY ASSURANCE PROJECT

A.Y.S. Chau, Project Chief

INTRODUCTION

The mandate of the Quality Assurance (QA) Project is to heighten awareness with respect to the need for a coordinated quality assurance program and to contribute expertise as needed to ensure that analytical data generated for Environment Canada are of good comparable quality. The Project is essential for successful management and utilization of water resources and for research on water pollution, particularly in the areas of toxic chemicals and acid rain. The ability of Environment Canada to provide authoritative and reliable scientific advice on control and remediation strategies is crucially dependent on the availability of high quality scientific data.

Chemical and biological data are essential to all decisions made by government with respect to environmental assessment and pollution control. Biased measurements can lead to errors in assessment and in subsequent control actions. In addition, the expense of data collection and interpretation makes the cost of discarding questionable data very high; therefore, data must be compatible, reliable and suitable for the intended use. A comprehensive QA program is the essential first step in the gathering of reliable data for use in environmental assessments. As its long term goal, the QA Project strives to assist in the development of comprehensive quality assurance programs in all relevant sectors of the Department.

As the lead body responsible for quality assurance, the QA group:

(a) plans, coordinates, and implements quality assurance and control programs to ensure accuracy, comparability and reliability of analytical data,
(b) develops and prepares Certified Reference Materials [CRMs] (water, sediment and biota) and reference materials for use in quality assurance and analytical methods research and environmental assessment studies,
(c) provides a consultation service on QA to Environment Canada, other federal departments, provincial agencies, and international establishments.

Typical project activities include the design and conduct of various interlaboratory comparison studies as well as the provision of support in the areas of methodology evaluation and

sample preservation for departmentally sponsored projects that have an analytical data collection component.

The QA Project is also initiating an active marketing component in advertising its products and expertise. In this regard, the first phase of the marketing activity is to advertise more aggressively the CRMs developed and prepared by the QA group. Also as resources and time permit, papers on QA and CRMs are presented at scientific conferences and symposia.

HIGHLIGHTS

The following paragraphs highlight special projects and activities carried out under the QA project but not addressed in individual study reports.

Dredging QA Program

Upon request from Public Works Canada and Environment Canada-C&P Ontario Region, the QA Group has become involved in a $30K project in support of the QA program associated with dredging activities within the Ontario Region. Under this project assistance will be provided to managers of the dredging projects in the choice of commercial analytical laboratories, with a view of ensuring that appropriate data quality is achieved.

Biomonitoring QA Guidelines

The QA Project has played a key role in the organization and chairing of a committee that has been given the mandate to develop a set of biomonitoring QA guidelines. The committee is made up of representatives of provincial and federal government agencies and private sector companies.

A workshop was organized and held at CCIW, February 20-21, 1990, to discuss and review several key topics on QA/QC in Biomonitoring, with the revision of a draft document on the subject constituting the main item of discussion. Some 30 participants representing public and private sectors interests contributed their expertise to the workshop. A final draft of the discussion document is under preparation.

Technical Transfer and Consultation

The QA group provides a leading role on QA matters through active participation (Chairman or appointed members)in multi-agency national and international bodies such as the QA Committee of the Association of Official Analytical Chemists (AOAC), the Dioxin QA

Committee of the DOE Dioxin Task Force, the Data Quality Work Group of the IJC and the Canadian Advisory Committee on QA Management of the International Standards Organization (ISO). In addition, expert advice on QA/QC matters is provided on a regular basis in response to requests originating from within and outside the Department.

Extensive advice and consultation were provided to the Ocean Dumping Advisory Committee, Environment Canada C&P-Pacific and Yukon Region, on matters pertaining to Quality Assurance in dioxin/furan analysis. QA project staff collaborated in the development of a detailed QA protocol that should be applied to dioxin/furan analysis data as part of the review of permit applications for the ocean disposal of marine sediments.

HYDRAULICS STUDIES PROJECT

M.G. Skafel, Project Chief

INTRODUCTION

Fluid dynamics and the interaction of water with air, sediments, shores and man-made structures are fundamental to many of the issues being addressed in the environment. The staff of the Hydraulics Studies Project address selected topics in wave mechanics, coastal, and fluvial engineering to provide new knowledge for use by water resource managers and engineers in Environment Canada and elsewhere. Special attention is given to understanding hydraulic processes that could lead to structural failure with serious environmental consequences.

The research program in wave mechanics creates new knowledge for the determination of accurate parameters related to fluxes of mass, momentum, energy and heat across the air/water interface. This work has direct consequences in understanding toxic gas transfer, diffusion of pollutants, wave prediction, lake circulation, seasonal thermocline development, weather forecasting and climatic change.

The coastal engineering program is focused on advancing the understanding of wave mechanics and sediment transport in the coastal zone, such as the resuspension of cohesive sediment, prediction techniques to develop wave climate models for sediment resuspension studies, shoreline evolution, and wave-structure interaction.

The fluvial engineering program is directed at improved understanding of fluid mechanics, sediment transport in rivers, the development of new and improved techniques for monitoring river processes, and flow-structure interaction with special emphasis on cases where structural failure could lead to serious environmental consequences. Emphasis is placed on providing information for operational branches in Environment Canada. Results are often applicable to issues in other departments and to other water resources managers.

The Hydraulics Studies Project operates the Hydraulics and Sedimentology Laboratories and provides technical support to Institute scientists and engineers using these facilities. The Project also encompasses the National Calibration Service, charged with current meter repair and calibration, primarily for the Water Survey of Canada.

A lead role is taken by Project staff in technology transfer to other government departments, universities, and the private sector. The facilities of the laboratory, when not committed to Institute activities, are actively marketed so that these other agencies have the opportunity to use our facilities as a resource in their activities. The client projects undertaken are primarily in the realms of fluvial and coastal engineering, and in the calibration of current meters.

HIGHLIGHTS

The project is actively supporting the Water Resources Branch program by conducting applied research studies addressing specific issues. Recent work includes: evaluation of an acoustic current meter; development of a new calibration equation for the Price current meter which improves the measurement accuracy at low flows; the development of a calibration strategy for suspended sediment samplers as well as the design and construction of a suspended sediment nozzle test facility; assistance in the development of a research program to measure flows under ice.

In view of the need to minimize the chance of oil spills from submarine pipelines in the Beaufort Sea, pipelines will be laid in trenches to avoid scour due to ice floes. Model tests completed in the hydraulics laboratory have indicated that forces due to waves on a pipeline in a trench can be approximated by forces on a pipe on a flat bottom at the same total depth. This finding means that design for wave forces can make use of the extensive literature available for flat bottom situations.

A monitoring program was undertaken by Transport Canada to determine the effects of the breakwater extension on water depths at an adjacent river mouth and marina. The hydrographic data were examined and no adverse effect was found. However, an unexpected result was revealed: the harbour area is undergoing subsidence due to a salt mine under the area. Transport Canada and Public Works Canada have been advised of the implications for ongoing maintenance of the harbour structures.

Gas transfer at the air-wave interface plays an important role in the global biochemical cycle. Recent experiments in the new air-tight recirculating gas transfer flume have examined the influence of small scale wave breaking (which is pervasive in open waters, in contrast to white-capping which is intermittent) on the transfer of a liquid phase controlled compound (chlorobenzene). It was found that the transfer rate increased dramatically under conditions where small scale wave breaking began. While other studies have reported the enhancement of the mass transfer velocity

in terms of wind speed, this study parameterized the mass transfer velocity in terms of the wind and wave properties.

Preparation for the surface waves dynamics experiment (SWADE), sponsored by the U.S. Office of Naval Research are proceeding on schedule for the first intensive experiments in the autumn of 1990. A team, lead by Mark Donelan has been developing instrumentation systems for five meteorological and wave direction buoys, as well as a wave direction system to be integrated onto a large spar buoy. A prototype wave direction and flux buoy was tested in the Gulf of Mexico. The main objectives of the experiment are to understand the dynamics of the evolution of the wave field in the open ocean, and to determine the effect of waves on air-sea transfer of momentum, heat, and mass.

The hydraulics laboratory and sedimentology laboratory were operated and technical support provided by project staff to scientists and engineers at NWRI. Current meters were calibrated and repaired in support of the Water Resources Branch. The project also takes a lead role in technology transfer by making available the facilities of the laboratories to outside clients on a fee for service basis. A biannual newsletter was distributed to persons interested in hydraulics research at NWRI.

I. ANALYTICAL CHEMISTRY RESEARCH

Study 84006: The Operation of the Mass Spectroscopy Laboratory

by*

H.B. Lee, K. Terry and R.J. Wilkinson

INTRODUCTION

Mass spectrometers are presently the most versatile and powerful tools in the analysis and confirmation of trace organics in environmental samples. Although many smaller quadrupole mass spectrometers are in use at CCIW for simple and routine applications, these units have low resolution and lack the flexibility of providing different ionisation techniques and different sample introduction and interface. In order to support analytical services and research activities of more demanding mass spectral requirements, a mass spectroscopy laboratory was set up and a VG Tribrid mass spectrometer was acquired, jointly with NWQL, on a lease-to-own basis.

RESULTS

The VG Tribrid is a medium resolution hybrid instrument incorporating magnetic sector, electrostatic sector and quadrupole analyzers. The instrument was chosen primarily because of its flexibility to satisfy the various research needs within NWRI as well as the requirements for routine dioxin analysis by NWQL. Although the instrument arrived in late 1988, it was not properly set up by the manufacturer until the end of August 1989, because of a few hardware problems and the lack of a workable software. During the installation period, samples were analyzed to confirm that factory specifications were met. For instance, an injection of 1 pg of 2,3,7,8 -tetrachlorodibenzo-p-dioxin (TCDD) at a resolution of 2000 produced a signal-to-noise (S/N) ratio of 10:1 using six ions. Because of hardware problems with the quadrupoles, MS/MS experiments on dioxins were not completed. Fully satisfactory results have been obtained in the analysis of pentafluorobenzyl (PFB) esters of resin and fatty acids with the Tribrid under negative ion chemical ionization (NICI) conditions and using methane as a reagent gas. The instrument is being evaluated for alternating electron impact(EI) and chemical ionization(CI) conditions in analyses of dioxin/furan.

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* In collaboration with J. Carron (NWQL)

Study 84006 (continued)

Investigative GC/MS analyses of complicated sample extracts, automated operation, and thermo- or plasma-spray LC/MS analysis are also being studied.

Delays in the acquisition of the Tribrid and problems encountered during its installation have hampered the efforts to reach the full operational capability of the instrument. At present, the complete NBS library is still unavailable and there is no provision to generate user-created libraries using the existing software. The electronic boards used to control and operate the quadrupole analyzers are to be exchanged for a newer version for improved performance. The EI and CI source assembly also needs upgrading for better serviceability. Various additions have been made to the system, namely a VAX 3000 computer and a second terminal to increase sample throughput and a VG particle beam interface for LC-MS. The system is currently used to support the quantitation and confirmation of dioxins in fish samples.

Study 84007: Electrokinetic and Enzymatic Detection of Subcellular Toxic and Mutagenic Effects

by

S.A.Daniels

INTRODUCTION

The evaluation of pollutants in terms of their toxic, carcinogenic and mutagenic effects is largely confined to the determination of mortality, the occurrence of tumors, and of imperfections in offspring. It is appropriate then to look "below the surface" to determine what causes these adverse effects. The development of laboratory techniques to routinely determine and characterize compositional and physiological changes in genetic and associated protein substances, would provide the capability to screen, categorize, and regulate environmental contaminants with a much greater appreciation for their potential detrimental effects.

To achieve these objectives, standard DNA preparations are selectively disrupted by specific enzymes to enable the laboratory detection and quantitation of resulting gene changes by electrokinetic protein differentiation procedures. With these techniques perfected, specific contaminant effects on DNA and other biomolecules will then be evaluated using the same methods. The conditions would then have been established for the application of these methods to the assessment of contaminant effects in aquatic organisms.

The goals of the research carried out in the current study are:(i) to establish a laboratory and the capability to effectively characterize low and high molecular weight proteinaceous material; (ii) to develop laboratory facilities for applying appropriate techniques to the characterization and analysis of nucleic acids; (iii) to evaluate the ability of these procedures to detect mutagenetic phenomena.

RESULTS

The laboratory is now adequately equipped and functional. Techniques of protein separation and analysis have been established. Good separations based on molecular weight have been achieved using preparations of myosin, phosphorylase (b), bovine serum albumin, ovalbumin, carbonic anhydrase, trypsin inhibitor, and lysozyme. Gradient and uniform SDS-polyacrylamide gels have been employed in these electrophoretic procedures. Southern electroblot gel-transfer techniques have also been established.

Study 84007 (continued)

To accelerate the process of establishing the laboratory capability to analyze, characterize and manipulate nucleic genetic material, technology sharing arrangements have been put in place for collaboration between S. Daniels and Dr. Allan Bernstein of the Mount Sinai Research Institute. As a result, first hand experience has been obtained with current clinical investigative practices in the areas of DNA and nucleic acid isolation, gene analysis and sequencing as means of detecting and characterizing mutagenesis. Methods employed in gene splicing and cloning as well as the use of DNA probes in analysis and investigations were also explored.

The modification of some of these techniques for application to environmental investigation is currently underway as part of this study.

To further boost our analytical and exploratory capabilities, a High Performance Capillary Electrophoresis system has been acquired and installed. This approach represents the very latest in electrokinetic separation technology and will be very helpful in improving the quality and precision of biomolecular analysis.

As part of a joint project with the NRCC Atlantic Research Laboratory, the use of ion-spray mass spectroscopy will be investigated for the identification and detection of DNA products. The specific objectives of the study are to evaluate (a) the applicability of ion-spray mass spectrometry for identifying DNA adducts, and (b) the potential of interfacing the capillary zone electrophoresis and HPLC with ion-spray mass spectrometry for use in the detection of DNA fragments.

Densitometry software has been acquired and incorporated within the analytical system to assist in the acquisition, organization and analysis of data.

Publications

Daniels, S.A., M. Munawar and C.I. Mayfield. 1989. An improved elutriation technique for the bioassessment of sediment contaminants. Hydrobiologia 188/189:619-631.

Study 84008: Development of Liquid Chromatographic Multi-Detection Technique Systems

by

B.K. Afghan and R.J. Wilkinson

INTRODUCTION

This new study has been initiated to explore the analytical potential of hyphenated liquid chromatography for the characterization, identification and determination of environmental pollutants at micro- and ultra-trace levels. Until recently, liquid chromatography (LC) has been used extensively in biochemical and biomedical application where relatively polar compounds are analyzed in biological matrices. High pressure liquid chromatography (HPLC) incorporating multi-detection technology offers great potential for the analysis of environmental samples. The method allows the separation of complex mixtures with constituents ranging from volatile to non-volatile and with molecular weights spanning over 3 to 4 orders of magnitude. The potential of HPLC is relatively greater for semi-polar and polar compounds because the parameters affecting the separation (the stationary and mobile phases) can be varied over a wide range of polarity and chemical functionality. In addition, the analytical measurements to obtain quantitative, multi-dimensional and fingerprinting information can be greatly improved by linking liquid chromatography to a wide range of detection techniques such as refractive index measurements, Fourier transform infrared spectroscopy, fluorescence, electrochemical techniques and mass spectrometry.

The objectives of this research project for the future are: (i) to automate and validate HPLC multi-detection system as part of the development of analytical methods for screening as well as measuring specific compounds at trace and ultra-trace levels; (ii) to explore the potential of pre- and post-column derivatization to improve selectivity and sensitivity for the detection of chemical and biochemical constituents in environmental samples, effluents and solid wastes.

RESULTS

A number of HPLC systems are being set up for the analysis of substances such as PAH, carbamates and organo-sulfur compound. Each system will be linked to a different detection technique and operating conditions will be optimized to obtain maximum selectivity and sensitivity.

Study 84008 (continued)

A literature search was carried out to review the current information available for over 100 different industrial chemicals and various pesticides. The literature search covered areas such as use, properties, occurrence and analytical methodologies with special reference to HPLC.

Preliminary performance verification of LC-MS was undertaken by analyzing selected candidate compounds deemed to be representative of the following classes of substances: organochlorine compounds, organo-phosphorus insecticides, carbamates, triazines, phenols, amines and PAHs.

Two HPLC systems were linked to UV/electrochemical and Photodiode array-fluorescence detectors, respectively. Phenols, amines and carbamates compounds have been used to examine the performance of the UV/electrochemical detector.

This study has been interrupted since mid-November, 1989 due to the illness suffered by the principal investigator, B.K. Afghan.

Study 84011: Supercritical Fluid Extraction and Chromatography

by

F.I. Onuska and K. Terry

INTRODUCTION

The use of supercritical fluids for the extraction of organic substances and its application to environmental analysis are being investigated under this study since 1988-89. Recent results from studies on the extraction of polychlorinated biphenyls (PCBs) have demonstrated a wide range of possibilities for this extraction technique. The work currently underway will examine various aspects that need to be addressed in the development and evaluation of a SFE-GC system, namely design, construction, interface, detection systems and automation.

RESULTS

Tandem Supercritical Fluid Extraction - High Resolution Gas Chromatography

A simple method has been developed for the direct coupling of supercritical fluid extraction (SFE) with a high resolution gas chromatography (HRGC) system using electron capture detection (ECD). SFE conditions have been investigated for the quantitation of PCBs and dioxins in terms of mobile phase, entrainer, pressure, temperature and mass-flow through the extractor. The dynamic leaching and static steady-state extractions were compared. Extraction efficiencies of up to 100 percent have been obtained with the procedure, requiring less than 15 minutes for PCBs and about 30 minutes for 2,3,7,8-TCDD. The extracted analytes are quantitatively transferred into a fused silica pre-column accumulator for HRGC analysis. The advantages of the SFE-HRGC methodology come from the possibility of combining the sample extraction and analysis steps in one system and to automate the operation of the system for rapid analysis of samples. Also the methodology brings improvements in safety aspects associated with the analysis of hazardous substances. The work carried out under this study provides information on the qualitative and quantitative aspects of the SFE-HRGC system for the extraction of sediments.

Feasibility Study on the Application of Photoionization detector for Supercritical Fluid Chromatography

The feasibility of incorporating a photoionization detector (PID) in a supercritical fluid chromatography (SFC) system

Study 84011 (continued)

has been examined. Faster acceptance of SFC is limited by the lack of detection systems more sensitive than those based on UV absorbance or flame ionization. This situation is nearly achieved when analysing hydrocarbon mixtures with a flame ionization detector (FID). In the case of more complex mixtures, selective detectors have to be used, for instance an electron capture detector for halogen-containing analytes and a flame photometric detector for sulphur- and phosphorus- containing analytes. We evaluated the performance of the HNV model P152-02 PID. From published data it is seen that the PID can be more selective than the flame ionization detector (FID) and the selectivity can be altered by changing the photon source. However, there is no data describing it performance with supercritical fluids. Under the supercritical fluid conditions the basic Beer-Lambert law equation must be modified and it can be written as

$$I = I_o \exp\left(\frac{\varepsilon}{n} \cdot P \cdot \frac{273}{T} \cdot X\right)$$

where, P is the pressure; T is the temperature; I is the intensity of light passing through the cell containing an analyte having an extinction coefficient ε; n is the Loschmidt's number ($2.69 \cdot 10^{25}$ vol/m^3 at STP) and X is thickness of the cell.

It was found that the SFC-PID system is effective for detection of compounds containing a phenyl ring. The optimal use of a PID requires that negligible excitation-absorption and electron capture rates be excited to have an acceptable sensitivity, even for aromatic compounds in supercritical fluids.

As a first conclusion, PID performance in SFC does not match the sensitivities obtained in gas chromatography. Our results confirm that the PID is only modestly sensitive to aromatic compounds. It can be used with both packed and microbore packed columns in SFC. However, the commercially available PID-detector is not suitable in its present design to be used with capillary SFC.

Tandem Supercritical Fluid Extraction(SFE)-Mass Spectromery (MS)

As part of our attempts to design an interface for a SFE-MS system, the preliminary results obtained have proved disappointing. Very poor sensitivity has been achieved and the system does not show promise for use in routine analysis. Further work in this area will not be pursued on account of the major

Study 84011 (continued)

engineering problems that would need to be solved to overcome the difficulties encountered so far in the development of a useful SFE-MS System.

Publications

Onuska, F.I. and K.A. Terry. 1989. Supercritical Fluid Extraction of 2,3,7,8-TCDD from Sediment Samples. J. High Resolut. Chromatogr., 12; 357-361.

Onuska, F.I. and K.A. Terry. 1989. Supercritical Fluid Extraction of PCBs in Tandem with HRGC in Environmental Analysis. J. High Resolut. Chromatogr., 12:527-531.

Onuska, F.I. and K.A. Terry. 1989. Identification and Quantitative Analysis of N-containing Polycyclic Aromatic Hydrocarbons in Sediments. J. High Resolut. Chromatogr., 12:362-367.

Onuska, F.I. and K.A. Terry. 1989. Quantitative HRGC and Mass Spectrometry of Toxaphene Residues in Fish Samples. J. Chromatogr., 471:161-171.

Mudroch, A., F.I. Onuska and L. Kalas. 1989. Distribution of PCBs in Water, Sediment and Biota of Two Harbours. Chemosphere, 18:2141-2154.

Presentations

Onuska, F.I. Supercritical Fluid Extraction as a Novel Analytical Tool in Environmental Samples Preparation. Presented at the 10th International Symposium on Capillary Chromatography, Riva del Garda, Italy, May 21-25, 1989.

Onuska, F.I. Microbore Columns vs. Open Tubular Columns for SFC in Environmental Analysis: Separation of Polychlorinated Biphenyls and Terphenyls. Presented at the COLACRO III Congress at Aqua del San Pedro, Brazil, March 13-17, 1990.

Study 84012: Preconcentration for Ultra-trace Analysis

by

D.H.J. Anthony

INTRODUCTION

Several activities of Environment Canada's Inland Waters Directorate(IWD) require the identification and quantitation of toxic organic contaminants in water at "ultra-trace" (ppt, ppq) levels. These activities include background level monitoring, agreement monitoring (e.g.,. Niagara River Toxics Management Plan) and pathways studies. For many of the "target" organic contaminants of current concern as well as for compounds likely to be investigated in future broad spectrum analysis studies, conventional analytical techniques cannot provide the sensitivity required for accurate identification and quantitation. Research conducted in this study endeavors to provide practical contaminant preconcentration techniques whereby the contaminants in a sample may be concentrated to a level permitting unambiguous and accurate determination by conventional instrumental techniques (e.g., GC-MS, GC-ECD). Research is continuing on the development of the large sample solvent extraction (LSE) technology, with emphasis on determining the suitability of supercritical fluid extraction (SFE) as a preconcentration technique for the activities mentioned above.

The following objectives have been established for the study during FY 89/90: (i) to investigate the modifications required to carry out specialized large sample extractions, including aspects linked to the extraction process and the extraction apparatus; (ii) to further develop LSE technology to improve routine use in a variety of laboratory and field applications; (iii) to study the feasibility of solid phase adsorption/supercritical fluid desorption as a preconcentration system for organic contaminants determinations.

RESULTS

Samples from experiments in large sample solvent extraction of "special" matrices such as pulp and paper mill effluents and bog water (high humic/fulvic acids content) have been analyzed. Results from bog water experiments suggested potential improvements to the method developed so far. A second field sampling was conducted in January 1990 and the analysis of the extracts obtained from this second sampling is currently in progress. Results from the study of large-sample extraction of pulp and paper mill effluents for the determination of chlorinated

Study 84012 (continued)

dioxins/furans have indicated a need for further sampling in order to improve aspects of the integration of this sampling technique with conventional cleanup-analytical procedures. Efforts will be made in FY 90/91 to obtain pulp and paper mill effluent samples for this purpose.

The assembly of a prototype large sample extractor, with solvent recovery incorporated as a feature, is near completion. The apparatus will be tested under field conditions at the Niagara-on-the-Lake monitoring station early in the 90/91 study period, through cooperation with staff of the WQB Great Lakes Surveillance Division.

A survey of recent research literature relating to the supercritical fluid extraction of environmental matrices has been completed. After a review of supercritical fluid technology equipment available commercially, components judged suitable for the objectives of this study were purchased.

The results obtained to date in this study, during field experiments with a variety of aqueous matrices, have led to the production of a commercial version of the Goulden Large-Sample Extactor (GLSE). As part of its marketing efforts, LaSalle Scientific Inc. of Guelph, Ontario, will attempt to identify and accomodate the interests of many water management organizations to use the LSE technology for particular applications. A commericial LSE unit was exhibited at the GLOBE '90 Trade Fair in Vancouver, B.C. as part of the NWRI contribution to Environment Canada's display.

Presentations

Anthony, D.H.J. An Overview of Field Applications of Large Sample Extraction Technology. Presented at the NWRI-MOE Methods Development Seminar, CCIW. Burlington, Ontario, May 24-25, 1989.

Anthony, D.H.J. Recommendations to the Prairie Provinces Water Board Committee on Water Quality Regarding the Application of Large-Sample Extraction Technology in the Development of a New Transboundary Water Quality Monitoring Program. Presented at the PPWB Water Quality Monitoring Workshop, Winnipeg, Manitoba, November 7, 1989.

Anthony, D.H.J. Exhibition of large-sample extraction technology featuring a recently marketed version of the Goulden Large-Sample Extractor. GLOBE '90 Conference and Trade Fair, Vancouver, B.C., March 19-23, 1990.

Study 84013: Continuous Flow Analytical Systems Research

by

I. Sekerka and J.F. Lechner

INTRODUCTION

The research work carried out under this study is focused on two general goals, namely to develop analytical methods as required by water quality assessment and to optimize the effectiveness and economy of environmental laboratories and environmental monitoring. The "Flow Injection Analysis (FIA) system" developed under previous research activities has been shown to meet the two goals stated above. FIA methods for Mg^{+2}, Ca^{+2}, Ba^{+2}, Na^{+}, B^{+3}, K^{+}, NH_4^{+}, NO_3^{-}, NO_2^{-}, PO_4^{-3}, CN^{-}, alkalinity and acidity are now used on a routine basis. In order to streamline certain aspects of FIA system such as increasing the rate of sample introduction into the system (up to 300 samples per hour), efforts have been devoted to the development of an automated robot system. In its final version, the robot system should handle entire strings of operations required for the analysis such as sample identification, sample delivery to the analyzer, operation of the analyzer, data collection, calculation of the results, statistical evaluation and storage of the data.

The following objectives have been established for the work carried out currently under this study: (i) examine the introduction of in-line systems into continuous flow automated analysis to improve the economy and efficiency of the preconcentration and digestion steps of the analytical procedure; (ii) a previously developed iso-thermal distillation system will be examined as part of the development of an automated continuous flow method for the determination of ammonia; (iii) progress in the robotization of analytical chemistry procedures will continue with the validation of the reliability of the developed system under long-term routine analysis conditions.

RESULTS

Analytical methods have been developed for the determination of ammonia and cyanide in a FIA system coupled to amperometric or conductometric detection.

Using a continuous-flow system, the species of interest (CN^{-} or NH_4^{+}) are converted to the gaseous state (by the addition of acid or base) for diffusion across a hydrophobic gas permeable

Study 84013 (continued)

membrane into a stationary collecting solution where the conversion to ionic form takes place. After some preselected time, this solution is pumped to the detector cell where the signal, amperometric for CN^- or conductometric for NH_4^+, is converted into a concentration of cyanide or ammonia in the sample on the basis of a calibration curve. The system is fully automated and can be linked to a main frame computer for data handling, evaluation and storage. Because the method is based on partial pressure, the results obtained are sensitive to factors affecting the Henry's Law constant that controls the volatization process.

The methods are interference free since they are based on the iso-thermal distillation principle. The ability to program the time of analyte collection allows to set the detection limits to suit a variety of situations depending on the type of analysis or samples involved.

An array of valves has been developed to permit in-line sample pretreatment and can be used in segmented and non-segmented continuous flow analysers. The filtration of the samples followed by the back-washing of the filter after each sample introduction can be carried out. The preconcentration and/or separation steps by sorption, ion-exchange, solid-liquid and liquid-liquid extraction, gas diffusion, osmosis, electrolysis and distillation can be executed. The desorption and regeneration of the cells and columns is also performed. A performance evaluation of the FIA based method for the determination of boron and ammonia in water has shown the valve system incorporated in our method to be reliable and efficient. The valve system contributes to the elimination of manual sample preparation steps that are often tedious and a source of error.

The robotic system developed earlier as part of this study has been installed in the NWQL for testing under routine analysis conditions. Good results and dependable performance have been obtained when the robot was used as part of a FIA-ICAP system for the determination of a variety of parameters. All the specifications set for the system, including an interface with a main frame computer, were achieved. The system was exhibited at the GLOBE '90 Trade Fair, in Vancouver, B.C., as part of the NWRI contribution to Environment Canada's display.

Efforts are underway by Radiometer for the marketing of a commercial version of the methodology developed previously under this study for the determination of the alkalinity or acidity of water.

Study 84013 (continued)

Publications

Sekerka, I. and J.F. Lechner. 1989. Automated Method for the Determination of Boron in Water by FIA with In-line Preconcentration and Spectrophotometric Detection. NWRI Contribution 89-83. Anal. Chem. Acta 1990, 234:199-206 1990).

Sekerka, I and J.F. Lechner. 1990. Analysis for Dissolved Oxygen in Natural Water Including Sample Preservation. NWRI Contribution 90-104.

Sekerka, I. and J.F. Lechner. 1990. Instruction Manual for the Determination of Na and K by FIA and Atomic Absorption Spectroscopy. NWRI Contribution 90-107.

Sekerka, I. and J.F. Lechner. 1990. Determination of Dissolved Oxygen by FIA. NWRI Contribution 90-109. Anal. Chem. (Accepted for publication).

Presentations

Sekerka, I. and J.F. Lechner. FIA Method for Boron Determination. Presented at the NWRI-MOE Methods Development Seminar, CCIW, Burlington, Ontario, May 24-25, 1989.

Sekerka, I. and J.F. Lechner. Automated Method for the Determination of Boron in Water by FIA with In-Line Preconcentration and Colorimetric Detection. Presented at the International Symposium on Detection in Liquid Chromatography and Flow Injection Analysis, Cordoba, Spain, September, 1989.

Sekerka, I. and J.F. Lechner. Iso-thermal Distillation in Continuous Flow Analysis. Presented at the Third International. Symposium on Kinetics in Analytical Chemistry, Dubrovnik, Yugoslavia, September 1989.

Study 84014: Broad Spectrum Analysis

by*

B. F. Scott

INTRODUCTION

The object of this study is to systematically group the peaks of non-target compounds in the chromatograms of environmental samples to obtain optimal information from the analysis of the samples. In this regard, particular attention is given to combining the optimization of gas-liquid chromatography(GLC) with advanced computer techniques. With the current routine GLC technology, target compounds usually contribute only a small fraction of the many compounds detected. As new approaches are developed for detector systems that can be coupled to gas chromatographs, these are investigated under this study for their potential to provide information on structural features of non-target compounds or to assist in the "finger printing" of samples collected as part of monitoring activities at particular sites. Efforts are also focused on the development of appropriate steps for the transfer of GLC results between computing systems for chemometric work on the data.

RESULTS

Participation in activities organized in response to two major environmental incidents (the suspected importation of tainted fuels into Ontario and the fire at a tire disposal site in Hagersville, Ontario) caused a significant realignment of the work planned under this study for the reporting period. This situation provided good cases to apply methodologies already developed or under development.

As part of the analytical work related to the tainted fuel incident, a large number of fuel samples needed to be analysed for PCBs and for the presence of organic sulphur(S)- or phosphorous(P)-containing compounds. The PCB analyses were carried out using dual capillary gas liquid chromatography(GLC) and electron capture detection, a method developed earlier under this study.

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* In collaboration with A. Cassista and R. Sampson (NWQL) and J.G. Zakrevsky (IWD-WQB-Regina).

Study 84014 (continued)

Chromatograms of all fuel samples were very complex and the method was very useful for confirming whether the PCB levels detected exceeded the regulatory 1 ppm level.

The requirement for the analysis of fuel samples to determine their possible contamination with S or P compounds was regarded as an ideal case for investigating the potential of an atomic emission detector (AED) in GLC analyses. The GLC-AED system has been recently introduced to the market place and has been promoted as particularly suitable for the element specific determination of various organic compounds in samples. Familiarization with this type of detector was gained through extensive work with solutions of S- and P-containing pesticides routinely analysed by NWQL. By using these pesticide solutions as standards in the analysis of fuel samples, it was shown that the method was capable of detecting S or P compounds at the 1 ppm level. Broad spectrum analysis techniques applied to the results obtained with the fuel samples indicated that only a few of the samples warranted further investigation for contamination by S or P compounds.

The GLC-AED system proved again very valuable in measuring for nitrogen(N) and Sulphur(S)-containing compounds in surface water extracts and other samples collected during the Hagersville tire fire.

On the basis of the work carried out to date with the GLC-AED system, ample evidence has been gathered to document the versatility, the specificity and the sensitivity of the method. This analytical tool can contribute useful information in the broad spectrum analysis environmental samples.

Publications

Scott, B.F., A. Cassista and R.L. Hong-You. 1989. Analysis of Contaminated Fuels. NWRI Contribution 89-129.

Scott, B.F. and F.I. Onuska. 1989. Analysis for Polychlorinated Biphenyls by Dual Capillary Column Chromatography. J. Microcolumn Separations, 1: 119.

Scott, B.F. and R. Szawiola. 1989. Comparison of Results Between PCB Congener Method and Standard Method Obtained During Validation Study. NWRI Contribution 89-9.

Scott, B.F. and A. Cassista. 1990. Analysis of Fuels for Possible Contamination by Organo Sulphur and Phosphorus Compounds using an Atomic Emission Detector. NWRI Contribution 90-106.

Study 84016: Operation of Clean and Hazardous Laboratory and Separation of Organic Substances

by

B.K. Afghan and R.J. Wilkinson

INTRODUCTION

Environmental monitoring for hazardous substances such as polychlorinated dibenzodioxins(PCDDs) and polychlorinated dibenzofurans (PCDFs) at ultra-trace levels (ppt and ppq) has increased significantly. The current programs and regulations related to PCDDs and PCDFs are anticipated to maintain a steady growing demand for the services of the Clean and Hazardous Chemical Laboratory (CHCL). The work under this study will continue to provide the necessary analytical reference data as well as to improve methodologies for the analysis of various congeners and isomers of dioxins and furans in environmental and related matrices.

RESULTS

As in previous years, there has been a steady demand for the specialized services of the Laboratory, with most of the work carried out involving the determination of levels of chlorinated dioxins and furans in water, sediment or fish tissue samples. A large portion of this work during the reporting period was related to on-going studies on the characterization of pulp and paper mill effluents. This area is the object of a high level of asessment and regulatory activity in the Department under the CEPA Priority Substances program.

The activities of the Laboratory provide support or assistance to studies carried out by various groups located at CCIW, as summarized below.

- study of the dechlorination of chlorinated dioxins and furans (NWRI-LRB);
- participation and assistance in Dioxin Interlaboratory QA studies (NWRI-RAB);
- operation of large volume water sample extractors (NWRI-RAB);
- development of supercritical fluid extraction/chromatography technology (NWRI-RAB);
- development of a dioxin reference material (NWRI-RAB);
- WQB-NWQL;
- Fisheries and Oceans/GLLFAS.

Study 84016 (continued)

A proposed reference method for the analysis of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in matrices related to pulp and paper mill effluents was documented. The protocol was developed in response to a request from the Industrial Programs Branch/C&P-Evironmental Protection and it proposes a method that could be used as part of the monitoring and control activities in the pulp and paper industry.

Publications

Afghan, B.K. 1989. Proposed Reference Methods for PCDDs and PCDFs. NWRI Contribution 89-128.

Study 84017: Screening Techniques for Toxic Substances

by

J.P. Sherry

INTRODUCTION

Conventional methods for the analysis of trace organic contaminants in environmental samples are generally time consuming and expensive. Often, many samples, eventually shown to be contaminant-free, must nevertheless be extracted and cleaned-up before being analyzed using GC or GC/MS. The inclusion of screening steps in analytical protocols would, by the elimination of contaminant-free samples from subsequent analysis, greatly reduce costs. Samples that test positive using the screening assay would be confirmed and quantified using conventional methods. Immunoassays (IAs) are among the most promising screening tests available.

Based on the classical antigen-antibody reaction, IAs are relatively simple, powerful and adaptable techniques for the rapid detection of trace levels of organic compounds. Most IAs cost about a few dollars per assay, although some commercially available kits can cost about $20 per sample.

Current research interests in this area at NWRI include the development of radioimmunoassay (RIA) techniques for PCDDs, and the determination of their performance characteristics with a variety of environmental matrices. Eventually it is hoped to have a battery of screening tests for the detection of a range of environmental contaminants.

RESULTS

The synthesis of a tyramine dioxin derivative (TDD) was completed and reported on at the Dioxin 89 Conference. Mass spectrometric analysis of this compound was undertaken. Several variations of the chloramine-T driven labelling reaction were evaluated using the TDD. The results were evaluated, and an improved hapten based on a histamine derivative of 2,3,7,8-TCDD was designed and synthesized.

An evaluation of an effective and efficient extraction and clean-up method for use in the analysis of PCDDs by Radioimmunoassay or conventional methods was completed and reported on at the Dioxin 89 Conference. The method replaces a time consuming liquid phase extraction procedure with a simple and rapid

Study 84017 (continued)

solid phase extraction. A multilayer column replaced three separate steps in the current clean-up procedure. No loss of performance was observed. This work included a comparison of the improved and existing extraction and clean-up procedures.

An RIA for PCDDs was developed using tritiated 2,3,7,8-TCDD as the tracer. Antiserum was calibrated and successful asssay calibration curves were prepared. This assay is promising. It addresses the following problems associated with our earlier RIA for PCDDs: the presence of inseparable hapten impurities and hapten instability. The tritiated assay is more sensitive than the earlier RIA: 50% response at 600 pg vs 5000 pg. Preliminary assay optimization results indicate the assay is capable of detecting 5 pg of 2,3,7,8-TCDD ($P<0.005$).

An activated charcoal separation system was developed for use with the tritiated TCDD based assay. Separation time was shortened from 6.5h to 35 minutes. The effect of assay incubation time and delayed tracer addition on assay performance were determined. Assay performance at low analyte levels was studied. Precision profiles were prepared for the assay using the charcoal and a second antibody based separation systems.

The development and validation of an immunoassay technique for the detection of triazine herbicides are nearing completion. The assay has been optimized, characterized and extensively tested using a variety of water samples. With the micro-plate version of the assay, a detection limit of 12.5 ppt was achieved without difficulty and an excellent dose response was achieved between 12.5 and 50 ppt. Good agreement was observed between the IA and GC results (correlation coefficient of 0.94). The results of this study were provided to Immunosystems Inc., to assist them with product development.

A rapid sample preparation technique was developed for use in conjunction with the IA screening technique. It is planned to complete the validation of this method in the coming year.

Publications

Sherry, J.P. 1989. A comparison of the abilities of 15 media to recover viable yeasts from pond, river and lake water. Journal Microbiological Methods, 10: 39-46.

Sherry, J.P. and H. Tse. 1989. A Procedure for the Determination of PCDDs in Fish. NWRI Contribution 89-133. Chemosphere (accepted for publication).

Study 84017 (continued)

Sherry, J.P., J.W. ApSimon, L. Collier, and P.W. Albro. 1989. Dimethyl Sulfoxide as Solubilization Agent in a Radioimmunoassay for the Detection of PCDDs. NWRI Contribution 89-130. Chemosphere (accepted for publication).

Presentations

Sherry, J.P. and H. Tse. An Effective and Efficient Extraction and Clean-up Method for the Analysis of PCDDs in Fish. Presented at the Ninth International Symposium on Chlorinated Dioxins and Related Compounds, Toronto, Ontario, September, 17-22, 1989.

Sherry, J.P., J.W. ApSimon, T.L. Collier and P.W. Albro. Further Development of a Radioimmunoassay for the Detection of PCDDs. Presented at the Ninth International Symposium on Chlorinated Dioxins and Related Compounds, Toronto, Ontario, September, 17-22, 1989.

Collier, T.L., J.W. ApSimon and J.P. Sherry. Development of an Improved Hapten for Use in the Radioimmunoassay of Dioxins. Presented at the Ninth International Symposium on Chlorinated Dioxins and Related Compounds, Toronto, Ontario, September, 17-22, 1989.

Sherry, J.P. Screening Techniques for the Detection of Environmental Contaminants. Presented at the NWRI-MOE Methods Development Seminar, CCIW, Burlington, Ontario, May 24-25, 1989.

Study 84018: Identification and Determination of Toxic Organics in Pulp and Paper Industry Effluents

by

H.B. Lee and T.E. Peart

INTRODUCTION

Pulp and paper industry effluents are known to be highly toxic to fish and other aquatic organisms. Among the toxic components, resin acids and some unsaturated fatty acids were identified as the major contributors to the toxicity in pulpmill effluents. While these acids and chlorinated phenolic compounds also found in the effluents have similar 96 hr LC_{50} values, the levels of the acids are often higher than those of the phenolics. The existing analytical methodology for the determination of resin acids is not sensitive enough for the monitoring of such acids in the many final effluents discharged into the environment. Thus there is a need to develop a more sensitive method for the determination and confirmation of resin and fatty acids (RFA) in pulpmill effluents.

RESULTS

Pentafluorobenzyl(PFB) esters were used in the analysis of RFA since these derivatives are easily formed, stable and have strong sensitivity in electron capture detection (ECD) systems. Separation of the PFB esters of all commonly found RFA was achieved by using gas chromatography with either a DB-5 or a DB-17 capillary column. RFA in effluents were extracted by methyl t-butyl ether, derivatized, and cleaned up on a silica gel column. Since the electron capturing PFB esters produce abundant and characteristic $(M-181)^-$ ions under negative ion chemical ionization (NICI) conditions, NICI mass spectrometry can be used in the confirmation as well as quantitation of RFA in effluents. Based on a 25 mL sample and a concentration factor of 10, the detection limit of the method was 1 µg/L for all acids.

Using this method, the RFA levels in the final effluents collected from 34 paper mills across Canada were determined. As many as 100 peaks were detected in a sample. Among the major acidic components, 30 or so were identified or tentatively assigned as fatty acids, *ca*. 15 as resin acids, another 20 to 30 as phenolics and the rest were unidentified. Among the saturated and unsaturated fatty acids found, straight-chain acids with an even carbon number from C_6 to C_{24} were always present with palmitic, stearic and oleic acids being the most abundant. For

Study 84018 (continued)

the resin acids, abietic and dehydroabietic acids were most prominent and were present in every sample. The chlorinated dehydroabietic and stearic acids were either undetected or present in insignificant amounts even in the effluents where high levels of chlorinated phenolics were found.

The total resin acid concentrations found in the effluents ranged from 49 to 7326 µg/L and were lower for the mills operating with secondary waste treatment. Using the effluent flow rate measured at each sampling site, loading of the toxic resin acids were estimated to exceed 500 kg/day for four mills and 100 kg/day for another five. Calculations of effluent toxicity on the basis of the RFA concentrations found suggested that 13 out of the 19 samples collected from mills without secondary treatment would be toxic to fish. Since high levels of RFA were found in some effluents, routine monitoring of these toxic acids is necessary for the protection of the fisheries and the environment.

Publications

Lee, H.B., T.E. Peart and J.M. Carron. 1989. Gas Chromatographic and Mass Spectrometric Determination of Some Resin and Fatty Acids in Pulpmill Effluents as Their Pentafluorobenzyl Ester Derivatives. NWRI Contribution 89-125; J. Chromatogr., 498:367-379 (1990).

Study 84019: Development of LC Methodology for Analysis of Environmental Samples

by

V. Cheam

INTRODUCTION

From an environmental analysis perspective, organic acids are relatively unknown compared to inorganic acids, partly due to the fact that they readily disintegrate, and therefore are not usually detected during analysis. Yet they are an integral part of the various processes forming the living environment and are present in most samples.

This study was focused on the development of a liquid chromatography(LC) methodology for the determination of organic acids in environmental samples. An evaluation of the Ion Exclusion Chromatography mode has been made first, followed by its comparison with Anion Chromatography modes. Data on precision, accuracy as well as overall ruggedness of the methods have been obtained and assessed.

RESULTS

Three methods were set up to study the seventeen acids potentially present in precipitation samples. The methods were isocratic anion exchange chromatography, ion-exclusion chromatography, and gradient anion exchange chromatography. The results show that (i) if only the more common organic acids (formic, acetic, propionic, butyric, lactic and glycolic) were of interest, the preferred method would be ion-exclusion chromatography, because it is more rugged and gives better peak resolution than the gradient mode; (ii) likewise, the isocratic anion exchange mode is preferred if only the more common inorganic acids (hydrofluoric, hydrochloric, sulfuric and nitric) were of interest; and (iii) if data on both type of acids are required, both the ion-exclusion and the isocratic anion methods have to be used concurrently, whereas only one gradient method is needed. Cost-effectiveness considerations favor the gradient method for simultaneously analysing mixtures of various organic and inorganic acids.

Study 84019 (continued)

Publications

Cheam, V. 1989. Determination of Organic and Inorganic Acids in Precipitation Samples. NWRI Contribution 89-93, J. Chromat., 482:381-392.

Cheam, V., K.I. Aspila and A.S.Y. Chau. 1989. Analytical Reference Materials. VIII. Development and Certification of a New Great Lakes Sediment Reference Material for Eight Trace Metals. Sci. Total. Envir., 87/88:517-524.

Presentations

Cheam, V. Simultaneous Analysis of Organic and Inorganic Acids in Precipitations Samples. Presented at the 6th International Symposium on ion chromatography, Sils-Maria, Switzerland, April 9-12, 1989.

Cheam, V. Organic and inorganic acids in rain samples. Presented at the NWRI-MOE Methods Development Seminar, CCIW, Burlington, Ontario, May 24-25, 1989.

II. QUALITY ASSURANCE

Study 84021: Organic Quality Assurance

by

Yvonne D. Stokker and A.S.Y. Chau

INTRODUCTION

The provision of interlaboratory Quality Assurance studies for various organic parameters is a valuable and very necessary service for any laboratory involved in environmental management, monitoring and surveillance, or research. Under this study, efforts are focused on the design, conduct, and interpretation of interlaboratory QC studies, in support of the Canadian Association of Pesticide Control Officials (CAPCO), the Federal/Provincial Quality Assurance Program, and the National Dioxin QA Program. As well, special studies are carried out under the National QA Program. Each participating laboratory receives a summary of all interlaboratory Data from which peer appraisals can be made. Precision and accuracy data can be determined for each laboratory when blind duplicates and CRMs are included among the samples distributed.

The effectiveness of interlaboratory Quality Assurance studies, interlaboratory Quality Control, and analytical methods research is strongly dependent on the availability and use of reference materials (RMs) and certified reference materials (CRMs). These may be analytical standards, either neat or in solution, sample extracts, or natural substrates such as samples of water, sediment or biota. They must be stable, well-characterized, and homogeneously subdivided into identical aliquots. Their matrices should be identical, or at least very similar, to those of the field program materials in order to eliminate or greatly reduce the matrix effect between reference and test samples. The target value for each parameter must be well established and supported by sufficient valid documentation. Each RM and CRM should be periodically monitored in order to ensure the stability of all parameters over time.

The major goals for the Organic QA Program this year were as follows, built around the two main elements of QA programs, interlaboratory QA/QC studies and the development of reference materials:

(1) to prepare reference samples in ampules for organic compounds;
(2) to provide assistance for two National Dioxin Interlaboratory QA studies;
(3) to initiate, design and conduct two interlaboratory QA studies for other organic QA programs (FICP/CAPCO, Fed/Prov);

Study 84021 (continued)

(4) to provide assistance in the screening of sediment CRMs for selected organic parameters; and
(5) promotion of QA products and expertise.

RESULTS

Reference Samples in Ampules

The preparation of reference materials in ampules was supported this year by funding from the PESTMYOP program.

A reference sediment extract was prepared by acetone-extracting 2.0 kg of freeze-dried sediment from Lakes Erie and St. Clair. The extracts were filtered, combined and concentrated until 1.0 mL of the extract represented 2.0 g of the original freeze-dried material. Previous work had revealed the presence in this material of approximately 100 ng/mL PCBs, 10-1000 ng/mL PAHs and 1-50 ng/mL chlorobenzenes. The extract was fortified with 1-5 µg/mL each of trifluralin, triallate, atrazine, alachlor and metolachlor. "Standard" solutions were also prepared to match the concentration levels in the sediment extract. In total, more than 1500 ampules containing these five neutral herbicides of interest were sealed. Homogeneity between the ampules was established and stability of the neutral herbicides was verified over a six-month period.

In addition to those of the neutral herbicides, ampules of standard solutions were prepared for several Aroclor blends, polynuclear aromatic hydrocarbons and for fenitrothion. These analytical reference standards in ampules were provided to many government laboratories, both federal and provincial, as well as to laboratories in the private sector in support of their research and monitoring programs and for in-house quality control check samples.

Interlaboratory Studies

A number of regular and special interlaboratory studies were organized and carried out under this study during the report period, in support of various programs as summarized below. Assistance was also provided for many aspects of two dioxin interlaboratory QA studies reported under Study 84027.

In a study being conducted under the auspices of CAPCO, (formerly the FICP National Check Samples Program), 26 laboratories across Canada were each sent a set of ampules containing five neutral herbicides in analytical standard solutions and in sediment extracts. The majority of the 15 laboratories who provided data

Study 84021 (continued)

were able to obtain results very close to the design concentrations for most parameters in each ample. This QC study is being conducted as part of the PESTMYOP study on sediment reference extracts in ampules.

One interlaboratory QA study for organic compounds was conducted for the Federal/Provincial Program. This year, eleven laboratories analyzed for total PCBs in injection-ready solutions in ampules. The results of this study were very encouraging as the interlaboratory medians were within 10% of the design values for all levels of analysis and only one of the eleven participants displayed serious problems with PCB quantitation.

Three special QA round-robin studies were also conducted this year in the course of activities surrounding specific incidents. The first study was carried out during the tainted fuel incident in May 1989 when there was a need to quickly assess the capability of particular laboratories to analyse for PCBs in fuel samples. The second special study was related to a suspected case of groundwater contamination by PAHs in New Brunswick. The results of a round-robin study carried out on the occasion indicated that while several Canadian laboratories are capable of performing sensitive analysis for several PAHs, this might not include the ability to accurately detect certain PAHs, such as benzo[a]pyrene, at the level of the drinking water guidelines. The third special study was requested by departmental staff in the Atlantic Region as part of an assessment of the results obtained by DOE Laboratories for fenitrothion analyses.

Promotion of QA Products and Expertise

As part of the efforts for marketing the QA Group's products and expertise, a brochure advertising NWRI's Certified Reference Materials has been distributed at several conferences, symposia, trade fairs and external QA meetings. Official "Certificates of Analysis" for the certified reference sediments and "Price Lists" for all the reference waters and reference and certified reference sediments have been printed for broad distribution.

Publications

Stokker, Y.D. and A.S.Y. Chau. 1989. Summary FICP Report: Interlaboratory Study on the Analysis of organochlorinatedInsecticides in Natural Waters. NWRI Contribution 89-97.

Stokker, Y.D. and A.S.Y. Chau. 1990. 1989/90 CAPCO Study Report: Interlaboratory Study on the Analysis of Neutral Herbicides in Sediment Extracts.

Study 84022: WQB, PPWB and Federal/Provincial Quality Assurance Programs

by

H. Alkema

INTRODUCTION

Quality Control Studies were initiated in the early 70's under request from the Water Quality Branch (WQB) as part of the ongoing interregional quality control program (IRQC). Presently, some 40 parameters in four water samples are sent out bimonthly to five regional WQB laboratories. Evaluation results for each bimonthly study are communicated quickly to the participating laboratories, usually within weeks after receipt of the data. Six QA reports are prepared each year.

For the Prairie Province Water Board (PPWB), a QA program was initiated in 1982 as an ongoing program because there was "a need to improve the compatibility of federal and provincial water quality data being collected in interprovincial and international streams in Western Canada". At present, three provincial laboratories (Alberta, Saskatchewan and Manitoba) and two WQB laboratories participate in the program. The IRQC QA program was expanded and modified to meet the PPWB objectives of assessing long term data comparability and to enhance in-house quality control programs in these provincial and federal laboratories.

In the latter part of the 1980's, under several Federal/Provincial WQ agreements, five more laboratories were integrated with the IRQC-PPWB program. In the past year, with the privatization of the B.C. Environmental laboratory, two private sector laboratories from that province have joined the Federal-Provincial program. At this time, a total number of 18 laboratories are involved in the Federal-Provincial and PPWB programs.

The laboratory results under these programs are tested in absolute terms with the use of certified reference waters. Generally, laboratories report their results in a timely manner and take corrective action when results are identified as anomalous. There are, however, several laboratories whose results continuously or intermittently fall in the poor performance area.

Study 84022 (continued)

RESULTS

The QA/QC studies conducted under the programs described above have resulted in the preparation and distribution of 13 preliminary data evaluation and 12 final reports. Additionally, three NWRI reports summarizing these final reports have been completed and published as NWRI Contributions.

A contract has been negotiated with the B.C. Ministry of Environment to cover the monthly delivery of reference (audit) samples to the Ministry as well as the participation of a contract laboratory involved in a verification role for data generated in that province under the Federal/Provincial QA program.

Special initiatives are underway to improve the technical aspects of this study. For example, an extensive computer program for automated data evaluation and flagging and the revised version of a major parameter dictionary revision have been developed and tested. Also work is progressing for the entry of archive data in a new S2K database which should be of great assistance for the preparation of precision and accuracy reports and laboratory performance assessments.

Three large volume reference waters were prepared for the Federal-Provincial QA program and for sales of reference water samples.

Publications

Alkema, H. 1990. Annual Report for the Inter-lab Federal-Provincial QA Program, Studies FP33-44 (Sept 88 - Aug 89) for Inorganic Constituents in Surface Waters. NWRI Contribution 90-110.

Alkema, H. 1990. Annual Report for the Inter-lab Prairie Provinces QA Program, Studies PP73-84 (Sep 88 - Aug 89) for Inorganic Constituents in Surface Waters. NWRI Contribution 90-111.

Alkema, H. 1990. Rapport Annuel RAQFP, Substances Inorganiques dans des eaux de surface, Études FP 31-44, juillet 1988 à août 1989. NWRI Contribution 90-112.

Study 84023: LRTAP Interlaboratory Quality Control Studies

by

K.I. Aspila, N. Arafat and A.S.Y. Chau

INTRODUCTION

The Federal-Provincial Long Range Transport of Atmospheric Pollutants (LRTAP) programs involve approximately 60 different laboratories that generate data on soft surface waters and precipitation samples. Many millions of dollars are invested in the laboratory production and use of these data. If these data are to be merged or used to define trends or acidic impacts, then these data must be unbiased and precise. This project helps define data quality, assists laboratories in taking corrective action and provides assistance to network managers who plan to merge data bases.

Studies for this project include ten soft natural waters that are distributed to normally 50 to 60 laboratories. Analyses are requested for about 20 constituents. Results are analyzed for measurement bias using the nonparametric approach of Youden. Individual results that deviate significantly from interlaboratory medians are flagged either high or low. Studies are normally completed about eight weeks after distribution. Each laboratory is then provided a laboratory specific appraisal indicating its performance. Corrective action is suggested when performance is poor.

RESULTS

This project has provided 20 interlaboratory comparison studies since 1982. In FY 89/90 three new studies designed to address major ions, nutrients and physical parameters were scheduled and completed.

The external QA program continues to demonstrate that laboratories can improve their performance when they participate frequently in an effective peer group audit program (the round-robins) and have a management attuned to Quality Management, Quality Assurance and Quality Control concepts.

Study 84023 (continued)

Data assessment procedures are now heavily automated and utilize both the mainframe computer at NWRI and microcomputers. A computer program to illustrate how interlaboratory precision varies with concentrations was prepared. By using the relationship developed in the program and data provided by "satisfactory" laboratories, criteria can be established for correctly flagging among the results of an interlaboratory study those that deviate from targets.

To reduce cost and labor, a manual has been prepared to describe how QA data files can be created and transmitted by phone modem into the Cyber computer at NWRI. When fully implemented in 1990, the electronic transfer system will significantly reduce labor costs.

Seven 200 litre volumes of highly characterized audit waters were developed, prepared and delivered to a private sector laboratory working under contract for the U.S. EPA. These soft water samples will be used to evaluate the performance of U.S laboratories generating analytical data under the American acid rain program.

Publications

Aspila, K.I. 1990. Overview of Quality Assurance in Laboratory Studies. Assessment of Quality Assurance in Studies Monitoring the Effects of Acid Deposition in the Canadian Environment. Section 9.5 of the RMCC 1990 Assessment Report. NWRI Contribution 90-134.

Aspila, K.I. and A.S.Y. Chau. 1990. On Assessing the Performance of Laboratories in Large External QA Programs. NWRI Contribution 90-135.

Study 84024: IJC Quality Control Studies

by

K.I. Aspila and A.S.Y. Chau

INTRODUCTION

Agencies that support the Canada-U.S. Great Lakes Water Quality Agreement routinely generate data on many environmental substrates. These analytical data are made available to the institutions of the International Joint Commission (IJC). To assist the users of this data, and to help assist laboratories in creating high quality data, the Data Quality Work Group organizes interlaboratory studies.

Studies are evaluated by the nonparametric techniques of Youden and Wilcoxan. These techniques provide powerful methods to discern laboratory measurement bias. Individual results that deviate significantly from interlaboratory medians are also flagged high or low.

RESULTS

During the reporting period, preparation work was carried out for the following three interlaboratory studies: total phosphorus in sewage treatment plant effluents, toxic organic compounds in ampules and trace metals in sediments. Samples for the phosphorus study have been distributed to participants and the project is at the results assessment stage. In the case of the other two studies, the sample distribution is on hold until the participant laboratories have been identified.

Study 84025: External QA For The Eulerian Model Field Study

by

K.I. Aspila and J. Lee

INTRODUCTION

The governments of Canada, the United States of America and Ontario as well as the Electric Power Research Institute in America are collecting daily rainwater samples in their respective precipitation networks covering a 24 month period started in 1988. Chemical analysis data from these four networks will be merged and the Eulerian model for atmospheric transport will be evaluated.

To assist managers of the Eulerian Model Field Study Program, the QA group in the Research and Applications Branch has arranged to provide monthly interlaboratory performance evaluation studies. Participants in these studies include the four primary laboratories in the Eulerian program as well as four or five other laboratories. Each month these laboratories are provided ten precipitations samples for analysis of 14 specific constituents and their results are appraised for bias by the nonparametric method of Youden. Individual results that deviate significantly from interlaboratory medians are flagged high or low.

RESULTS

Following the practice established at the start of the QA program, laboratory specific appraisals continue to be mailed to each laboratory within four weeks of completing each study. Also the results of each study have been entered into a SYS2K data base management system for future retrieval and use.

The performance of the four primary laboratories is considered quite good and the operational management team has indicated great satisfaction about the ability of the QA program to demonstrate that the participating laboratories can produce comparable data.

The project included the preparation of low level (near detection limit) audit samples for daily analysis by each laboratory. This special study originally carried out in the spring of 1989 has been requested again and a new set of samples were prepared and delivered. These 10 litre samples were repetitively analyzed and used by each laboratory to re-evaluate their detection limits.

Study 84025 (continued)

When this project terminates in July 1990, 14 studies will have been completed. All the results data accumulated will then be analysed and a formal overview report will be prepared.

Precision functions that illustrate how interlaboratory standard deviation varies as a function of concentration have been established. These relationships can be used successfully in interlaboratory study results to readjust the criteria on the basis of which individual results that deviate from target values can be flagged.

Publications

Aspila, K.I. and W.C. Li. 1990. Preparation of Low Level reference Samples for the Eulerian Model Evaluation Field Study. NWRI Contribution 90-137.

Aspila, K.I. and A.S.Y. Chau. 1990. On Assessing the Performance of Laboratories in Large External QA Programs. NWRI Contribution 90-135.

Study 84026: QA For the Canadian National Pulp Mill Dioxin Monitoring Program

by

Alfred S.Y. Chau

INTRODUCTION

At the time when the concept of a National Pulp Mill Dioxin Sampling Program was being developed by the Canadian Pulp and Paper Association (CPPA), Environment Canada, upon request from the Association, accepted the responsibility to organize the QA/QC aspects of the program on a cost-recovery basis. As a result, the QA Project Chief was asked to assist the Environment Dioxin Task Force by constituting and chairing a QA Committee to support the CPPA's dioxin sampling program.

The Dioxin QA Committee (DQAC) was formed in September 1988 and has taken on as its main role the provision of advice to the CPPA and DOE Dioxin Task Force on the adequacy of procedures used for collecting, preparing, shipping and analyzing samples for dioxin and furan determinations and on the acceptability of individual analytical results.

RESULTS

A detailed QA protocol was developed and finalized by the DQAC as a working document specifically intended for the CPPA Monitoring Program. Since it is the only detailed document of its kind available at this time, the protocol has also been adopted within the DOE sediment monitoring program and the Ocean Dumping Program of EP (Pacific & Yukon Region).

Seventeen sets of analytical data and chromatograms obtained from work on pulp, effluent and sludge samples were extensively revieved by the DQAC members to ensure that the QA protocol is followed and the data are of suitable quality.

The evaluation of all the data generated is now completed.

Presentations

A.S.Y. Chau. Essential Ingredients for Environmental Assessment and Research: CRMs & RMs. Presented to the 4th International Symposium on Biological and Environmental Reference Materials, Orlando, FL. February 5-8, 1990.

Study 84027: CEPA QA

by

A.S.Y. Chau, W. Li and Y.D. Stokker

INTRODUCTION

The successful implementation of various aspects of the Canadian Environmental Protection Act (CEPA) is critically dependent on the availability of reliable scientific data. These data are essential to all decisions made by the government with respect to environment assessment, pollution control and enforcement of legislation. In this context, the QA Project has initiated a new study to provide timely assistance on QA/QC matters to operational programs focused on the implementation of CEPA, particularly those dealing with enforcement and compliance activities.

RESULTS

Interlaboratory Study for Dioxins and Furans

Two interlaboratory studies centered on the determination of dioxins and furans in sediments were designed and conducted; 11 laboratories provided results in the first study and 12 laboratories in the second study. In each study, participating laboratories were requested to analyse 4 sediment samples for a variety of dioxins and furan congeners, particularly the 2,3,7,8-tetrachloro isomers. The results of these studies will provide information about the capability of the laboratories to generate sensitive and accurate analytical data for dioxins and furans determinations.

Sediment Reference Materials for Dioxins and Furans

In efforts to prepare reference materials for use in dioxin and furan analysis, investigations are continuing to identify a suitable source of contaminated sediments. A suitable site in Western Canada has not yet been found due to insufficient levels of dioxins or inappropriate matrix (such as too much pulp or oily materials for effective homogenization). As an alternative source, the large quantity of Lake Ontario sediments collected for the purpose of preparing reference materials contaminated with organic compounds were screened for dioxins. The bulk sediment was partially freeze-dried and plans are being made for its processing.

Study 84027 (continued)

Special QC Check Samples for Dioxins and Furans

In support to the national monitoring project for "Dioxins and Furans in Bottom Sediment from the Vicinity of the 47 Canadian Pulp & Paper Mills Using Chlorine Bleaching", a set of quality control samples were prepared to monitor the performance of contract laboratories involved in the analytical work.

Interlaboratory Study for Chorophenols

An interlaboratory study for chlorophenols in sediment extracts was designed and conducted. More than 30 laboratories participated. A final report is now in preparation.

Advice and Consultation

Extensive advice on QA and laboratory performance was given in support of the following programs: Ocean Dumping Program for Dioxin (Western & Pacific Region), Bottom Sediment Dioxin Monitoring Program (C&P, Headquarters); 3 B.C. Mill Dioxin Emergency Analysis (EP Headquarters); MISA program (Ontario Ministry of the Environment [MOE]).

Extensive review and advice was provided on the compatibility of dioxin/furan data generated by MOE and private sector laboratories to establish the feasibility of combining these data into an Environment Canada report currently under preparation.

III. HYDRAULICS STUDIES

Study 84031: The Surface Wave Dynamics Experiment (SWADE)

by

M.A. Donelan

INTRODUCTION

The following objectives have been set for the work carried out under this study: (i) to understand the dynamics of the evolution of the wave field in the open ocean; and (ii) to determine the effect of waves on air-sea transfer of momentum, heat and mass.

RESULTS

The SWADE experimental plan is now set. The array of surface measurements consists of one spar buoy, five meteorological and wave directional buoys, four meteorological buoys in addition to seven existing meteorological buoys in the area, which is just east of Wallops Island, Virginia. The airborne systems include five aircraft and one airship. It is also possible that the European Research Satellite ERS-1 will be launched during the SWADE experimental period (1 October 1990 to 31 March 1991), thereby providing additional wind and wave information in the SWADE area and the adjoining Atlantic Ocean Basin. The most advanced numerical wave models will be used during SWADE and they will be driven by analysed wind fields supplied by the U.S. National Meteorological Center, the European Centre for Medium Range Forecasts and the Fleet Numerical Oceanographic Center of the U.S. Navy.

The prototype SWADE wave directional and flux buoy was tested against data from a fixed tower in the Gulf of Mexico. Excellent agreement of the wave measurements with the tower data was found. The buoy has been returned to the Gulf for further tests of its flux measuring systems. The analysis of these preliminary tests are being conducted with F. Anctil, a Ph.D. student from Laval University.

A paper, describing the scientific plans for SWADE and a related experiment (SWAPP), has been prepared in collaboration in the R.A. Weller and M.G. Briscoe.

Study 84032: Fluvial Engineering

by*

P. Engel

INTRODUCTION

The fluvial engineering study is directed at improved understanding of fluid mechanics, sediment transport in rivers, the development of new and improved techniques for monitoring river processes and flow-structure interaction with special emphasis on cases where structural failure could lead to serious environmental consequences. Emphasis is placed on providing information for operational branches in Environment Canada. Results are often applicable to issues in other departments and to other water resources managers.

The work in this study is divided into three categories. Branch research consists of studies conducted as part of the long term research plan of the Research and Applications Branch (RAB). Joint research covers studies that are consistent with the RAB long term research plan and carried out under joint funding arrangements with partners from governmental (federal, provincial and municipal) agencies and the private sector. Cost recovery research covers term studies, site or product specific, and is funded totally by the client in accordance with the Treasury Board guidelines.

RESULTS

Support to Water Resources Branch

Acoustic Flow Meters

The work on the development of an acoustic flow meter by the Water Survey of Canada (WSC) continued. The final report on the tests conducted on the Stork Flow Meter, designed in Holland, has

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* In collaboration with T.L. Lau and S.G. Krishnappan (NWRI-SRS); M.O. Spitzer (WRB-Calgary); I. McLaurin, E. Wiebe and P. Szymiak (WRB-HQ); S. Tassone (WRB-Vancouver); S. Wagner (USGS, Reston, Virginia); D. Doede (RAB).

Study 84032 (continued)

been completed. The report dealing with the properties of the flow meter, an error analysis and the hydrodynamic aspects of testing acoustic flow meters in a towing tank has been accepted by WSC staff.

Vertical Velocity Profiling

Work on a method to measure the mean velocity for flows with irregular vertical velocity profiles was continued. The preliminary tests in the two meter flume have been completed and the data have been analyzed. The method will make it possible to measure flows in river cross-sections where standard methods do not apply. A report has been completed and is being reviewed within WSC.

Calibration Equation for Price Current Meters

A new form of calibration equation, based on physical principles, has been developed for rod supported meters and has been shown to improve measurement accuracy at low flows. A study report has been submitted to and accepted by WSC.

Effect of Suspension Assemblies on Price Meter

A study was conducted to isolate the effect of winter weight assemblies on the performance of a Price meter. Knowledge of the effect can be used to improve current meter calibration. A study report has been prepared and submitted to WSC.

Research Program to Measure Flows Under Ice

Work was completed on the development of guidelines for a comprehensive experimental measurement program at 36 hydrometric sites across Canada. The work was conducted with WSC through its Committee For Measurement of Flow Under Ice. A report was prepared on the criteria for selection of suitable river cross-sections for the implementation of the measurement program. The report has been accepted by WSC.

Calibration Strategy for Suspended Sediment Samplers

The draft report on the short term and long term research requirements for the development of a calibration strategy was accepted by WSC. Work was conducted on the implementation of the short term research. A sampler nozzle test facility was designed and fabricated with WSC funds. Performance tests were successful.

Study 84032 (continued)

The report on this facility and on results of the performance tests was accepted by WSC.

Milk River Weir Model

Development of the prototype design was initiated. Tests are under way to develop an efficient and economical stilling basin to protect the structure against scour. Report on the modelling of the stilling basin and the final design recommendations will be completed early in the next fiscal year.

RAB Research

Flexible Roughness in Open Channel Flow

The literature survey on the resistance to flow and fine sediment trapping characteristics of vegetated channels and river flood plains was begun. The work will be continued in the next fiscal year.

Vortices at Pump Intakes

Work was completed jointly with RRB on a review of physical modeling of free surface vortices at pump intakes. This work was done to develop the required expertise in physical modeling on cost recovery projects. The information gathered in this review has been assembled into an internal report.

Characteristics of Bed Load Samplers

A brief report was prepared to summarize previous work by the Hydraulics Laboratory on bed load sampler tests. The document examines the relationship between hydraulic and sampling efficiency of basket type samplers used by WSC. The information contained in the report should be useful to WSC as well as to potential cost recovery clients.

Cost Recovery Research

Gibson Lake Power House Physical Model

A detailed proposal was submitted to Sandwell Swan Wooster, Consulting Engineers, on the design and construction of a physical model to conduct tests on the approach flow conditions to a proposed hydroelectric low head power facility near Thorold, Ontario. After considerable consultation, the client did not

Study 84032 (continued)

proceed with the study because Ontario Hydro's initial requirement for a model was waived.

Testing Acoustic Flow Meters

A proposal consisting of a test program and cost estimates was submitted to Ramsay Lake Industrial Limited. Acceptance of the proposal is pending.

Bed Load Sampler Calibration

A request was received from Ontario Hydro to provide a standard calibration for their Bogardi type samplers. After several discussions and careful assessment of the client's sampling problems, it was decided that calibrations would not be in their best interest.

Manning's "n" from Model Tests

A report was prepared in which model and prototype values of Manning's "n" are compared. The results show that values obtained from model measurements can significantly underestimate the true values. The data was retrieved from previous cost recovery work with permission of the client. The report provides information for future cost recovery work.

Publications

Fast, E.J., P. Engel and K. Wiebe. 1989. Preliminary Laboratory and Field Evaluation of the AFFRA Acoustic Flow Meter. Water Resources Branch Technical Report.

Engel, P., Y.L. Lau and M.O. Spitzer. 1989. Effects of Bed Level Fluctuations on Discharge Measurement in Alluvial Streams. NWRI Contribution 89-88.

Engel, P. and Y.L. Lau. 1989. Laboratory Tests of Artificial Control for the Milk River - Phase II. NWRI Contribution 89-92.

Engel, P. and P. Zrymiak. 1989. Development of a Calibration Strategy for Suspended Sediment Samplers - Phase I. NWRI Contribution 89-121.

Engel, P. 1989. A New Calibration Equation for Vertical Axis Current Meters. NWRI Contribution 89-131.

Study 84032 (continued)

Engel, P. 1989. Criteria for the Establishment of an Experimental Program for the Measurement of Flows in Rivers with Solid Ice Cover. NWRI Contribution 89-132.

Engel, P. 1990. Effects of Winter Sounding Weight Assemblies on the Performance of the Price Current Meter. NWRI Contribution 90-100.

Engel, P. E.J. Fast and K. Wiebe. 1990. Towing Tank Tests of the Stork 1500 MMRI Acoustic Flow Meter - Final Report. NWRI Contribution 90-105.

Engel, P. 1990. Comparison of Model and Prototype Values of Manning's"n" for Artificial Roughness Elements. NWRI Contribution 90-114.

Engel, P. 1990. A New Facility for the Testing of Suspended Sediment Sampler Nozzles. NWRI Contribution 90-116.

Engel, P. and Y.L. Lau. 1990. Physical Modeling of Free Surface vortices at Pump Intakes - a Review. NWRI Contribution 90-119.

Presentations

Engel, P., Y.L. Lau and M.O. Spitzer. 1989. Effects of Bed Level Fluctuations on Discharge Measurements in Alluvial Streams. Presented at the 9th Canadian Hydrotechnical Conference of the Canadian Society for Civil Engineering, St. John's, Newfoundland, June 8-10, 1989.

Study 84033: Coastal Engineering

by

M.G. Skafel, C.T. Bishop, M.A. Donelan and J. Doering

INTRODUCTION

The objectives of this study are to develop techniques and models for wave prediction, shoreline evolution, wave interactions with the bottom such as resuspension of sediments, and wave-structure interaction.

RESULTS

Shoaling Waves

The analysis of the field data in terms of the joint probability density function of heights and periods of shoaling waves has been completed. The first laboratory runs, using a beach with a slope of 1:40 in the wind-wave flume, have been completed. Experiments are now underway to explore the velocity field and energy dissipation in shoaling waves using a three-dimensional acoustic current meter.

One-dimensional Wave Hindcasting

The comparison study of four one-dimensional wave hindcasting techniques is completed. The main emphasis of the work recently has been to compare the direction estimating capabilities of the models with field data from Lake Erie, Lake St. Clair, and the Gulf of St. Lawrence. Significant differences have been found, and are being examined.

Two-dimensional Wave Prediction Model

As part of a comparison of wave climate models, a two-dimensional model developed by M.A.Donelan has been investigated. Differences were observed between predictions of NWRI's version of the model HAMSP and a version modified at the Great Lakes Environmental Research Laboratory (GLERL). This led to a detailed 'debugging' analysis by J. Hodson (RSD), now completed. Comparison runs with measured data and with one-dimensional models have been undertaken, and the results are being analyzed. A report on both the one- and two-dimensional techniques is in preparation.

Study 84033 (continued)

Submarine Pipelines

Wave forces on submarine pipelines in trenches were studied in the laboratory. The trench configuration is the same as proposed for use in the Beaufort Sea, where trenches are required to place the pipelines below the draft of ice floe keels. It was found that the forces were similar to those reported in the literature for pipes on flat beds at the same total water depth.

Great Lakes Water Level Variations

The rejection in 1988 by the Journal of Great Lakes Research of a manuscript submitted by Bishop has prompted further research and more development of the ideas and has resulted in a thorough revision of the manuscript. In late 1988, a paper was published by others in the Cdn. J. Earth Sci. which purports to show a climate-induced oscillation in the level of Lake Ontario over the last 3300 years, with an amplitude of about 1 m and a period of several hundred years. Bishop's research indicates that the climate-induced variations in mean annual levels of the modern Great Lakes have probably not exceeded those on record since measurements began in 1815. A paper discussing this data was submitted by Bishop and Coakley (LRB) and has been published.

The revised manuscript on "Historical Variation of Water Levels in Lakes Erie and Michigan-Huron" has been accepted by the Journal of Great Lakes Research. Several oral presentations based on the publication were made to various audiences.

Goderich Harbour Environmental Monitoring

A monitoring program was undertaken for Transport Canada, starting in 1984, to determine changes in water depths at Goderich Harbour which may have been caused by a rubblemound breakwater constructed in 1984-85. Results of the hydrographic survey conducted in 1988 were examined. These results, combined with those from 1984, 1985 and 1986, indicated a general lowering of the lake bottom in the survey area, even at water depths of 10 m where negligible changes were anticipated. Consequently, C. Bishop and P. Zrymiak (WSC) held discussions with officials of Domtar Ltd. concerning the lowering (subsidence) of the bottom of Lake Huron in the vicinity of the company's salt mine. It now appears that a total subsidence of 30 to 50cm due to mining activity in the survey area has occurred since 1984. Preliminary results and implications for Transport Canada have been discussed at two meetings held at the offices of Public Works Canada in North York.

Study 84033 (continued)

A final study report has been completed and a case study paper based on these results has been accepted for presentation at the Canadian Coastal Conference 1990.

Miscellaneous

At the request of Public Works Canada, Ontario Region, C. Bishop undertook a brief cost recovery study to review reports concerning waves used for the design of a rubblemound breakwater at Bronte Outer Harbour. In particular, wave shoaling techniques from linear and TMA theories were compared. A letter report was sent to Public Works.

C. Bishop responded to a number of requests for information concerning floating tire breakwaters (FTB's). A marina operator near Picton, Ontario has expressed an interest in building FTB's commercially. Technology transfer to the individual through provision of reports and advice is ongoing. Public Works Canada is interested in the feasibility of using an FTB to provide wave protection as part of rehabilitation efforts at the CCIW offshore breakwater. A physical hydraulic model study of wave transmission and force characteristics of the CCIW breakwater, with and without an FTB, is underway in the NWRI Hydraulics Laboratory.

At the request of EP-Ontario Region, C. Bishop reviewed a consultant's report on sedimentation in Frenchman's Bay at Pickering. Also, M. Skafel and C. Bishop reviewed several coastal development proposals.

At the request of the Grand River Conservation Authority, M. Skafel and C. Bishop visited Conestogo Lake to observe a critical shore erosion site. Recommendations and information regarding bank stabilization methods were given to the Authority.

At the request of the Ontario WP&MB, M. Skafel made a presentation to the East Pelee Littoral Cell Shoreland Management Plan Steering Committee on Coastal Processes in the East Pelee Littoral Cell.

Publications

Skafel, M.G. and C.T. Bishop. 1989. Flow Visualization Around a Pipeline in a Trench. NWRI RAB Technical Note: RAB TN-89-06.

Skafel, M.G. and C.T. Bishop. 1989. Wave Forces on a Pipeline in a Trench. NWRI Contribution 89-122.

Study 84033 (continued)

Bishop, C.T. and J.P. Coakley. 1989. Stratigraphy of the Sixteen Mile Creek Lagoon, and its Implications for Lake Ontario Water Levels: Discussion. Can. J. Earth Sci., 26: 1074-1076.

Bishop, C.T. and M.A. Donelan. 1989. Wave Prediction Models. in: Applications in Coastal Modeling, V.C. Lakhan and A.S. Trenhaile (editors), Elsevier Science Publishers B.V., Amsterdam, 75-105.

Bishop, C.T. and P. Zrymiak. 1990. Impact of the Rubblemound Breakwater at Goderich Harbour on Coastal and Fluvial Processes. NWRI Contribution 90-121.

Study 84034: Wave Mechanics

by

M.A. Donelan

INTRODUCTION

The objectives of this study are to discover or develop theories and/or models to describe and predict the interaction of wind and water, including surface waves; fluxes of mass and energy; turbulence; and orbital velocity beneath breaking waves.

RESULTS

The Lake St. Clair data provides an unusually detailed view of wave growth and decay along a line of five towers spaced roughly at 5 km intervals on a bearing of 294° True. Previous attempts to derive fetch-limited growth laws have yielded conflicting results and no consensus can now be said to exist. We argue that this is largely due to differences with wind along the time of the fetch. Systematic increases in wind speed occur as the low level wind adjusts to the greatly reduced roughness as it propagates from land to water. Thus systematic biases in fetch laws will occur depending on fetch length (adjustment distance) and upstream (land) roughness. A more consistent approach is to examine differences in wave energy between two offshore stations sufficiently close together that the wind is much the same as both stations. One may thus derive a fetch law in differential form that is free of the above mentioned biases. This has been successfully done (with M. Skafel, S. Venkatesh, H. Graber, P. Lin and D. Schwab) and a fetch-limited "law" has been retrieved that includes the hypothesized asymptotic approach to full development. A paper describing these results is in preparation.

Engineers have long been troubled with the difficulty of estimating orbital velocities near the surface of wind-generated seas. The literature contains at least six semi-theoretical approaches, none of which is generally regarded as satisfactory; the simple ones failing in accuracy, the more sophisticated ones in having excessive computational requirements. In collaboration with a doctoral student François Anctil, another method has been developed that is both simple and accurate. The method has been compared to existing methods and is currently being tested against actual data obtained using an acoustic current meter on a wave-follower on the research tower in Lake Ontario during an earlier year (1987) component of this study. Data obtained

Stucy 84034 (continued)

in a wind-wave flume as part of the "Shoaling waves" Component of Study 84033 were also used. A paper based on this research work is in preparation.

The directional spectrum analysis is in progress and yielding several interesting results. The work is being done by M. Donelan (NWRI), I. Tsanis (McMaster University) and K. Kahma (Finnish Marine Research Institute). A paper has been published and three more are in preparation.

Numerical simulation of nonlinear wave group propagation has been successfully implemented up to maximum envelope steepness of 0.3. The results will be presented at the 11th Annual Conference of the Canadian Applied Mathematics Society and published in the conference proceedings.

The crucial work on the separation of waves and turbulence in the increased subsurface velocity has been successfully tested and the analysis of the data (starting with 1987) is under way. Concurrent analysis of the data from our drag spheres (2 sensors) and the U.S. acoustic current meters (12 sensors) permits continuous cross-checks. The team of scientists involved in this task consists of: M. Donelan (Study Leader), W. Drennan (Post-doctoral fellow), K. Kahma (Finnish Marine Research Institute) and E. Terray (Woods Hole Oceanographic Institution). The interpretation of results is focused on four main areas: (1) momentum flux estimation; (2) the kinematic energy balance; (3) velocity structure of the mean surface layer; and (4) comparison of measurement and theoretical orbital velocities and accelerations.

Work has begun on establishing the individual terms of the kinematic energy balance in the atmospheric boundary layer over water waves and a paper describing the apparatus and methodology has been prepared.

A considerable part of the effort in this study was devoted to the writing of a review paper on "Air-Sea Interaction" for The Sea, Volume 9.

Publications

Donelan, M.A. 1990." Air-Sea Interaction" The Sea, Vol.9: Ocean Engineering Science. Eds. B. LeMehauté and D. Hanes. Wiley and Sons. pp. 239-292.

Tsanis, I., and M. Donelan. 1989. Air-Water Interaction Experiments in Lake Ontario. Proc. Canadian Congress of Applied Mechanics (CANCAM).

Study 84034 (continued)

Presentations

Tsanis, I. and M. Donelan. Wave Directional Spectra in Mixed Seas. Presented at the 2nd ESRF International Workshop on Wave Hindcasting and Forecasting, Vancouver, April 1989.

Study 84035: Transfer of Toxic Gases

by

M.A. Donelan

INTRODUCTION

The objective of this study is to establish the dependence of the transfer of toxic gases at the air-water interface on the parameters of the interface.

RESULTS

The gas transfer flume was thoroughly tested and met or exceeded all its specifications having maximum centreline wind speeds of 24 m/s and 10.5 m/s in the circulating and vented configurations respectively. The current speed can be varied between 0 and 60 cm/s. The three profiling stations are in place and are capable of automatic profiling at steps of 1/40 mm. Menu-driven software for the profilers' micro-processor has been prepared and tested. The laser wave height and slope gauges have been assembled and tested. Chemical sampling systems are in place. A non-dispersive infrared CO_2 and H_2O analyser has been purchased and a Fourier transform infrared analyser is on order.

A series of physical and chemical experiments to establish the mass transfer rate of organochlorine insecticides was conducted at various wind speeds. The physical experiments consisted of measurements of stress, heat flux, evaporation and wave spectra at three fetches. The chemical experiments consisted of gas chromatographic analysis of concentration of the pollutant in the water phase to establish the equilibrium concentration using fresh air (vented configuration) and a known rate of introduction of the pollutant to the water phase. A paper is in preparation and will be presented at the 2nd International Conference on Gas Transfer at Water Surfaces.

A full understanding of gas transfer of pollutants, for which the resistance to transfer is concentrated in the water phase, requires a careful study of the turbulence properties (particularly energy dissipation) just beneath the surface. Experiments have been conducted using hot wire anemometry to explore the profiles of turbulence properties within 15cm beneath the surface. Novel methods of determining the velocity profile to within 0.5mm of the surface are being explored.

Study 84036: National Calibration Service

by

B. Taylor, D. Fekyt, C. Bil and B. Near

INTRODUCTION

This study encompasses the NWRI's commitment to calibrate and repair all flow meters owned and used by the Water Survey of Canada (Water Resources Branch, Environment Canada). This work is organized and conducted through the National Calibration Service. In addition to the services provided to WSC, calibration and instrument repair services are made available to outside clients on a cost recovery basis.

RESULTS

For the 1989/90 fiscal year, 180 requests for services were actioned. A total of 796 calibrations and 512 current meter repairs were completed for WSC offices throughout the country, and for external clients such as universities, provincial or federal government agencies, hydro utilities, private companies, and 1 USA government agency. These requests resulted in revenues of $23.4K for 1989/90.

In order to ensure accuracy of the system, traceable to national standards the carriage is calibrated every 6 months. The overhead monorail hoist for handling heavy components to and from the carriage has been upgraded to improve efficiency and safety of operations.

Study 84037: Hydraulics and Sedimentology Laboratory Operations

by

B. Taylor and Technical Services Staff

INTRODUCTION

This study covers the support provided by specialized technical staff to hydraulics and geotechnical research and related activities carried out in the Hydraulics and Sedimentology Laboratories.

RESULTS

The human resources of the Technical Services Section were fully utilized to assist in NWRI mission research as well as cost recovery projects (see Study 84038). Technical staff have provided hydraulics laboratory and field support to several projects in all three research branches of NWRI. Staff were assigned to studies on a task by task basis and records of time utilization were maintained. All costs related to individual studies were assumed by the respective projects.

The newest addition to the Hydraulics Laboratory was the installation of a rotating flume for fine sediment studies by Dr. Krishnappan.

The Sedimentology Laboratory staff operated and maintained the large common-user freeze dryer and carried out size analysis on sediments for many clients at CCIW as well as for outside clients on a partial cost recovery basis. Appropriate arrangements have been completed to offer sediment analyses using a settling tube technique.

Study 84038: Applied Research and Engineering

by

C.T. Bishop and the Scientific, Engineering and Technical Staff of Research and Applications Branch and Rivers Research Branch

INTRODUCTION

This study covers all third party revenue activities carried out within the Hydraulics Studies Project. In addition, administration and technical support is provided to third party revenue work carried in the Hydraulics Laboratory and involving Study Leaders from the Rivers Research Branch.

RESULTS

The following list summarizes the cost recovery activities during fiscal year 1989/90. These activities generated funds totaling $84.4K.

Client	Project	Revenue
Various	carryovers 1988/89	$12,226
Various	National Calibration Service	$23,424
DPW, North York	Bronte Hbr. desk Study	$ 1,480
Mr. D. Campbell	snowmobile ski test #1	$ 1,100
Hayward Gordon Ltd	obs. tank rental (mixer)	$ 1,194
USEPA (K. Aspila)	coldroom rental	$21,024
DREO (Ross Pines)	tower rental	$ 3,774
Ramsey Lake Ind. Ltd	acoustic meters tests	$ 1,929
Mr. D. Campbell	snowmobile ski test #2	$ 1,950
Centre St.Laurent	Sed. Lab Support	$ 510
Gore & Storrie	Weir Calibration	$ 1,165
NWRI/DPW	CCIW breakwall	$15,000

At the request of NWRI-SSD, a 1:8 scale model of the CCIW breakwater was designed and constructed in the wave basin of the Hydraulics lab. The model study will provide information on wave forces exerted on the breakwater and on wave transmission past the structure; this information will be used by Public Works Canada to help design the rehabilitation of the breakwater. The use of a floating tire breakwater moored on the seaward side of the CCIW breakwater will also be investigated. The estimated completion date of the study is May 1990.

Study 84039: Hydraulics Laboratory Public Relations and Third Party Revenue

by

C.T. Bishop, M.G. Skafel, W.B. Taylor and P. Engel

INTRODUCTION

The following objectives are pursued under this study: to increase awareness in Canada and the U.S. Great Lakes region about the NWRI Hydraulics Laboratory capabilities and its availability for third party work; to improve means of accommodating and conducting third party work; and to increase third party revenue to the Laboratory.

RESULTS

Issues no. 2 and 3 of the Hydraulics Lab Newsletter were distributed during the reporting period. French and English versions of a promotional brochure on the Hydraulics Laboratory were revised, updated and printed.

A 1.2m long scale model of a Parshall flume was assembled for display as part of Environment Canada's participation at the GLOBE '90 Trade Fair in Vancouver, in March 1990.

Numerous tours of the Hydraulics Laboratory were offered during the past year to potential clients and scientists visiting CCIW.

APPENDIX

RESEARCH AND APPLICATIONS BRANCH

List of Personnel and Areas of Expertise

DIRECTOR'S OFFICE

Director

J. Lawrence, B.Sc., Ph.D. (Bristol)
[Analytical Chemistry and Quality Assurance]

Science Liaison Officer

R. Bisson, Ph.D. (Western Ontario)

Special Projects Coordinator

J.F. Ryan

Secretarial/Administrative

J. Burford
L. Heinrich
C. Kennedy
D. Weekes

QUALITY ASSURANCE PROJECT

Project Chief

A.S.Y. Chau, B.Sc. (British Columbia), M.Sc. (Carleton)
[Reference Materials and Quality Assurance]

Project Scientists

H. Alkema, B.T. (Ryerson)
[Federal/Provincial QA Program and Preservation]

K.I. Aspila, B.Sc., M.Sc.(Carleton)
[Quality Assurance]

Y. Stokker, B.Sc. (Guelph), M.Sc. (Queen's)
[Organic Method Development and Quality Assurance]

W.C. Li, B.Sc.(National Taiwan), Ph.D.(Wisconsin)
[Quality Assurance]

Technologist

N. Arafat, B.Sc.(Waterloo)

ANALYTICAL CHEMISTRY RESEARCH PROJECT

Project Chief

I. Sekerka, RNC., RNDR. (Prague), CSc. (Ostrava)
[Electroanalytical Chemistry and Continuous Flow Analysis]

Project Scientists

B.K. Afghan, B.Sc. (Sind), D.I.C. (I.C., London), Ph.D. (London)
[Liquid Chromatography]

D.J. Anthony, B.Sc. (McMaster)
[Spectroscopy and Sample Pre-Concentration]

V.F. Cheam, B.S., Ph.D. (Oklahoma)
[Ion-Chromatography and Spectroscopy]

S. Daniels, B.S., M.S. (Louisiana, Ph.D. (Waterloo)
[Electrokinetic Methods]

H.B. Lee, B.Sc. (Hong Kong), Ph.D. (McMaster)
[Gas Chromatography, GC/MSD and High Pressure Liquid Chromatography]

F.I. Onuska, P.Chem.Eng. (Bratislava), M.Sc. (Prague), CSc. (Brno), Ph.D. (Waterloo)
[Gas Chromatography, GC/MS and Separation Techniques]

B.F. Scott, B.Sc., M.A., Ph.D. (Toronto)
[High Pressure Liquid Chromatography and Gas Chromatography]

J.P. Sherry, B.Sc., Ph.D. (N.U.I.)
[Mycology and Radioimmunoassay]

Research Technologists

J.F. Lechner
K.A. Terry
R.J. Wilkinson

HYDRAULICS STUDIES PROJECT

Project Chief

M.G. Skafel, B.A., B.E., M.Sc. (Saskatchewan), Ph.D. (Cambridge), P.Eng.
[Coastal Engineering]

Project Scientists

C.T. Bishop, B.Sc., M.Sc. (Queen's), P.Eng.
[Coastal Engineering]

M.A. Donelan, B. Eng. (McGill), Ph.D. (B.C.)
[Air-Water Interaction]

P. Engel, B.A.Sc., M.A.Sc. (Waterloo), P.Eng.
[Fluvial Engineering]

Technologists

W.B. Taylor, Head, Technical Services Section

D. Beesley
C. Bil
J. Dalton
D. Doede
G. Duncan
F. Dunnett
D. Fekyt
J. Heidt
W. Moody
B. Near
T. Nudds
R. Stephens
B. Trapp
G. Voros